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## Clay nanotube encapsulation for functional biocomposites

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## ABSTRACT

Natural halloysite clay nanotubes with 50 nm outer- and 15 nm inner- diameters are described as miniature vehicles for sustained release of drugs and proteins. The release time may be adjusted from 10 to 200 h with the tube surface polymeric coating. An explanation of sustained release through locking electrical potential at the nanotube ends is suggested. These biocompatible ceramic tubes may be also used for architectural construction of nanoshells on microbes through alternation with polycations to enhance the intrinsic properties of biological cells. Halloysite nanotubes (pristine or drug-loaded) are well mixable with polar and low-polar polymers allowing for functional biocomposites with enhanced mechanical strength, adhesivity and slow release of drugs or other chemical agents. Halloysite is nontoxic abundantly available from natural deposit material which does not require exfoliation or other complicated energy consuming processing.

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## 1. Introduction

Halloysite clay is a natural tubule material formed by rolled kaolin sheets. Halloysite is aluminosilicate and is chemically identical to kaolin although usually contains minor amount of metal ions replacing in some positions aluminum. Typically 10–15 aluminosilicate layers roll into the cylinder and its wall packing may be controlled with (001) X-ray reflection of 0.72 nm for dry halloysite [1–4]. Surface of halloysite tubes is silica and its innermost is alumina, providing strong negative zeta-potential of ca. –30 mV on the tube surface and

+25 mV in the tube innermost in aqueous dispersions at normal pH. Halloysite tubes' diameter is of 40–70 nm with inner lumen diameter of 10–15 nm and length of  $1500 \pm 500$  nm (Fig. 1) [4–6]. It is interesting that sonication over a long time period of kaolin aqueous dispersion results in formation of halloysite-like tubes, though the product concentration is very low and the tube shape is rather poor [7]. An important advantage of halloysite as compared with platy clays like montmorillonite, kaolin and laponite stacked in larger crystallites is that these nanotubes do not need exfoliation and can be easily dispersed in water or polar polymers. Halloysite dispersion in water is stable for few hours and can be re-dispersed again with simple shaking or short sonication.

The size of halloysite tubes varies in different deposits, but smaller tubes providing slowest release kinetics are of the most interest and

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